Study of electrical properties of polycrystalline materials based on indium and copper selenides under high pressure

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Abstract. This paper discusses the influence of high pressures (up to 50 GPa) on the electrical properties of the polycrystalline materials $(InSe)_x(CuAsSe_2)_{1-x}$, $x = 0.05$ and 0.5. It was found that, for each compound, features in the pressure dependence of all the physical parameters of interest occur in the same pressure intervals, which can be due to structural transitions and a change in the electron structure.

1. Introduction

Multicomponent materials of the Cu-In-As-Se system are promising objects of investigation both from the theoretical and from the practical point of view because they exhibit a combination of interesting electrical, optical, magnetic, mechanical and other physical properties. In particular, at high pressures and low temperatures, they show negative magnetoresistance [1, 2], the causes of which have not been studied in detail. High-pressure structural phase transitions in these materials are also subject of investigations [2, 3].

This paper discusses the influence of high pressures (up to 50 GPa) on the electrical properties of the polycrystalline materials of $(InSe)_x(CuAsSe_2)_{1-x}$, x = 0.05 and 0.5, in direct (DC) and alternating current (AC) (1 Hz – 32 MHz) electric fields and in a transverse magnetic field ($0.2 < B < 1$ T). Magnetoresistance (MR) was calculated by the formula (1), where $R(B)$ is the electrical resistivity in a fixed magnetic field at a fixed pressure, and R_0 is the electrical resistivity at a corresponding pressure without magnetic field.

$$MR = \frac{R(B) - R_0}{R_0}. \tag{1}$$

2. Materials and experiment

The polycrystalline materials of $(InSe)_x(CuAsSe_2)_{1-x}$, x = 0.05, 0.5, were synthesized by melting high-purity initial components in quartz tubes evacuated to the residual pressure of 10^{-4} Pa and filled with superpure argon to $0.5{\cdot}10^5$ Pa. The details of the synthesis procedure are described in [4]. The X-ray structure analysis of the materials was carried out with Shimadzu XRD 6000 and Shimadzu XRD 7000 diffractometers (monochromatic radiation CuK_α). The $CuInAsSe_3$ ($(InSe)_x(CuAsSe_2)_{1-x}$, $x = 0.5$) compound crystallizes in tetragonal syngony with the chalcopyrite structure with lattice parameters a = 5.7967 Å and c = 11.5471 Å. The $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ compound crystallizes in the cubic sphalerite structure with a lattice parameter a=5.530 Å. At atmospheric pressure, the materials show the activation type of conductivity, and $CuInAsSe_3$ exhibits ferroelectric properties [4].

To apply high-pressure conditions, we used high pressure cells (HPC) with a rounded cone-plane-type anvil made of carbonado-type artificial diamonds. Such high-conductivity anvils make it possible to examine electrical properties of samples placed into HPCs [5]. A more detailed description of the pressure estimation and HPC calibration method is presented in [6]. The samples with a diameter of $\sim$ 0.2 mm and thickness from 10 to 30 μm were produced by compaction of initial powdered materials in HPCs. Electrical properties of the materials of interest in the pressure range of 15 to 50 GPa were examined by impedance spectroscopy in the frequency range of 1 Hz to 32 MHz using the Solartron 1260A universal frequency response analyzer. To measure the DC magnetoresistance, the high-pressure chamber was placed into a vertebrate magnet for generating a transverse magnetic field. Variations in the pressure and magnetic field were measured and controlled directly during the experiment.

3. Results and Discussion

Results of AC electrical measurements can be influenced significantly by electrode processes. This makes it necessary to differentiate the bulk response from the surface electrode processes. The analysis of the impedance frequency dependence allowed us to determine the frequency range, which characterizes the properties of the samples. The hodographs of impedance of both materials of interest are characterized by the presence of two clearly distinguished regions: high-frequency and low-frequency parts. The high-frequency parts of the hodographs are well approximated by semicircle arcs and characterize the properties of the materials, while the low-frequency part characterizes the electrode impedance. As pressure increases, the circle radii decrease for both materials.

A more careful analysis of high pressure effects on the electrical properties allowed us to determine the pressure intervals, where significant changes in the electrical properties occur. The real part of the impedance (ReZ) of $CuInAsSe_3$ begins to decrease fast when pressure exceeds 34 GPa, and at pressures above 37 GPa it does not depend on frequency anymore; all the $ReZ(P)$ curves merge at different electrical field frequencies. At 42 GPa, the ReZ value is about 270 - 280 Ohm; as pressure decreases, the ReZ values remain low and nearly constant (figure 1a). The electrical parameters of $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ have a similar behavior with significant changes at 23 - 24 and 38 GPa; at 45 GPa, the ReZ value is about 80 - 90 Ohm, as pressure decreases, the ReZ values remain low and nearly constant (figure 1b).

The curves of pressure dependence of the other electrical properties display features in the pressure range of 34 to 38 GPa for $CuInAsSe_3$ and around 24 GPa and 38 GPa for $(InSe)_{0.05}(CuAsSe_2)_{0.95}$. The high-frequency parts of the impedance for $CuInAsSe_3$ and $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ are characterized by arcs of semicircles at ambient pressure and up to 36 GPa and 24 GPa, respectively (figure 2). With a pressure increase above 36 GPa and 24GPa for $CuInAsSe_3$ and $(InSe)_{0.05}(CuAsSe_2)_{0.95}$, respectively, the high-frequency parts are approximated by practically vertical lines. The dielectric loss tangent for $CuInAsSe_3$ starts to grow at pressures above 37 GPa, and at pressures above 42 GPa it sharply rises. For $(InSe)_{0.05}(CuAsSe_2)_{0.95}$, the features of the dielectric loss tangent occur at pressures $\sim$ 24 GPa and $\sim$ 38 GPa. The AC voltage measurements show that the curves of electrical resistance versus frequency for $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ also have features near 24 GPa and 38 GPa. Such a behavior of the electrical properties may be connected with irreversible crystalline phase transitions in the materials of interest in the above pressure ranges. The results obtained for $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ agree with the results reported in paper [7], which studied high pressure effects on the electrical properties of the $(GeSe)_{1-x}(CuAsSe_2)_x$ materials. The possible

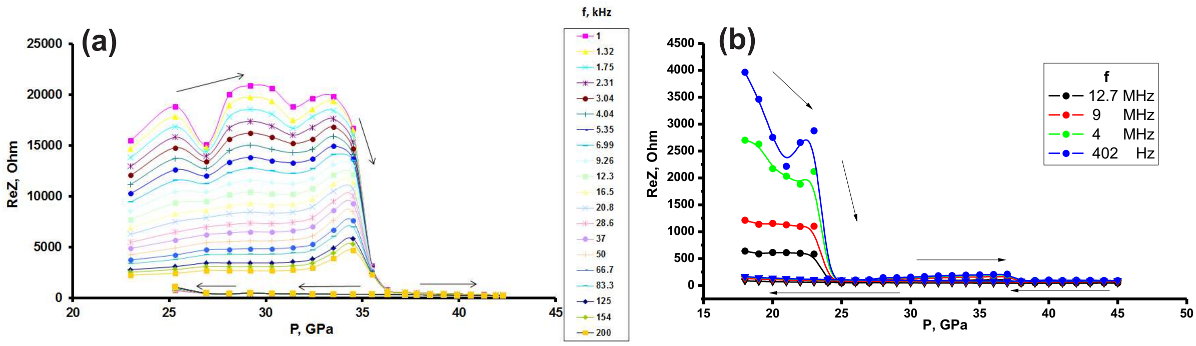

Figure 1. *ReZ* as a function of pressure for $CuInAsSe_3$ at AC in the frequency range from 1 to 200 kHz (a) and for $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ at AC in the frequency range from 400 Hz to 13 MHz (b). The arrows indicate the direction of the pressure change.

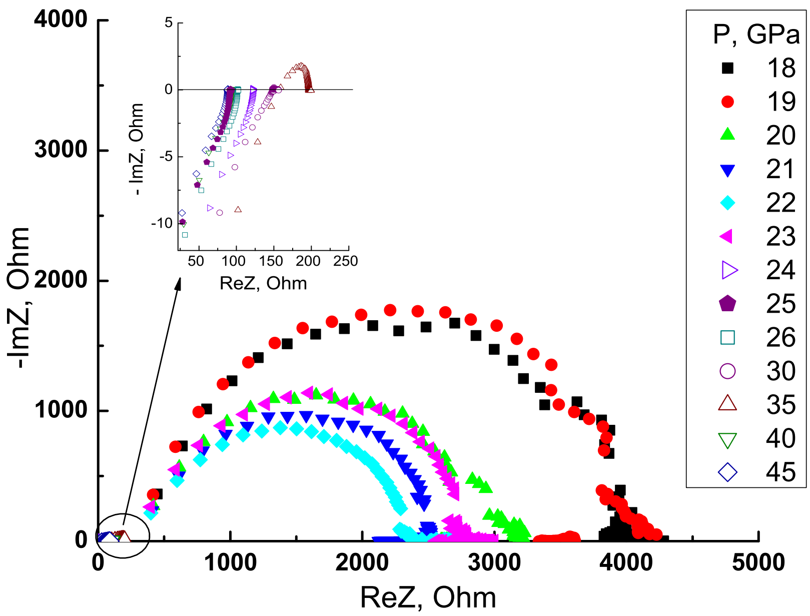

Figure 2. The impedance spectra of $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ at increasing pressure. The inset shows the hodographs of impedance at pressures above 23 GPa.

irreversible phase transitions accompanied by a rapid drop in resistivity with pressure growth were found in $(GeSe)_{1-x}(CuAsSe_2)_x$ for x = 0.9, 0.95 and 1.0 at pressures of 16 to 20 GPa, near 27 GPa and near 19 GPa, respectively.

The magnetoresistance of $CuInAsSe_3$ is negative in the whole pressure range of interest (figures 3 and 4). The mechanisms of scattering, which cause the negative magnetoresistance MR, are reviewed in [8]. The negative magnetoresistance is usually observed in semiconductors with a loose crystal structure, were the positive effect of MR is weak because of the small number

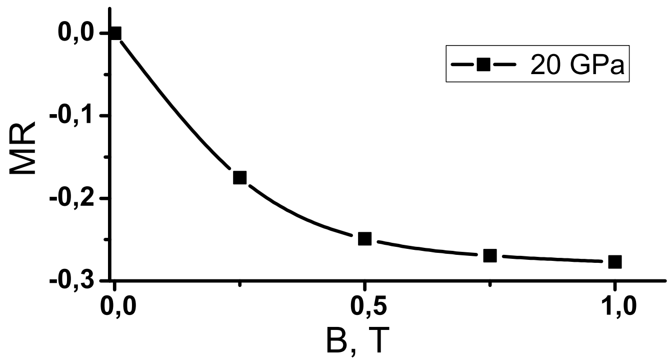

Figure 3. MR as a function of magnetic field for $CuInAsSe_3$ at pressure 20 GPa.

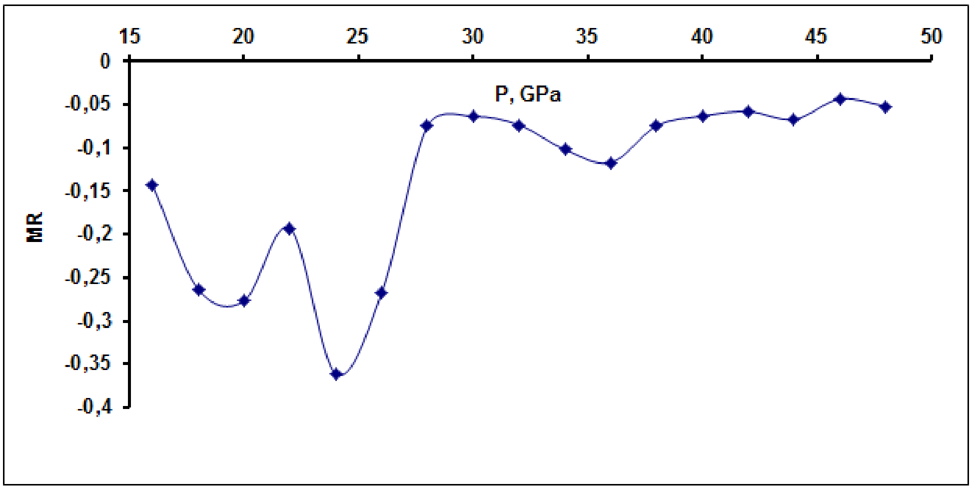

Figure 4. Magnetoresistance as a function of pressure for $CuInAsSe_3$ at $B = 1$ T.

of carriers. The magnetic-field dependence of negative MR caused by different mechanisms of scattering often has the same type: in weak magnetic fields, the dependence on B is quadratic; in strong magnetic fields, the effect has a tendency to saturation. The negative magnetoresistance effect can be due to low concentrations and mobility of carriers in the compounds of interest.

The pressure dependence of magnetoresistance for $CuInAsSe_3$ (figure 4) in a fixed magnetic field (B = const) is complex and similar to that of polycrystalline $CuInSe_2$ [2]. The curves of $MR(P)$ for both studied materials have some extrema (figures 4 and 5b). For $CuInAsSe_3$, one of the extrema is observed in the pressure range from 32 GPa to 40 GPa. In the same pressure interval, features were observed in the curves of pressure dependence of the dielectric loss tangent and imaginary and real parts of the impedance (figure 1a). The presence of the extrema in the $MR(P)$ curves can be due to crystalline phase transitions, like in the case of $CuInSe_2$ and $CuInS_2$ having the chalcopyrite structure and the lattice parameters close to those of the material under consideration at atmospheric pressure [2]. These transitions are accompanied by a decrease in the width of the energy gap, changes in the impurity band structure in the magnetic field, defect states, and changes in the concentration and mobility of carriers with gradual pressure growth. At pressures above ~ 38 GPa, the real part of impedance has small values, the magnetoresistance is small in modulus and practically does not change with further pressure growth.

The curves of $MR(P)$ for $(InSe)_x(CuAsSe_2)_{1-x}$, $x = 0.05$ (figure 5b), are similar to those of $CuInAsSe_3$. However, $(InSe)_x(CuAsSe_2)_{1-x}$, $x = 0.05$, crystallizes in another (sphalerite type) structure different from that of $CuInAsSe_3$ (chalcopyrite type) at atmospheric pressure,

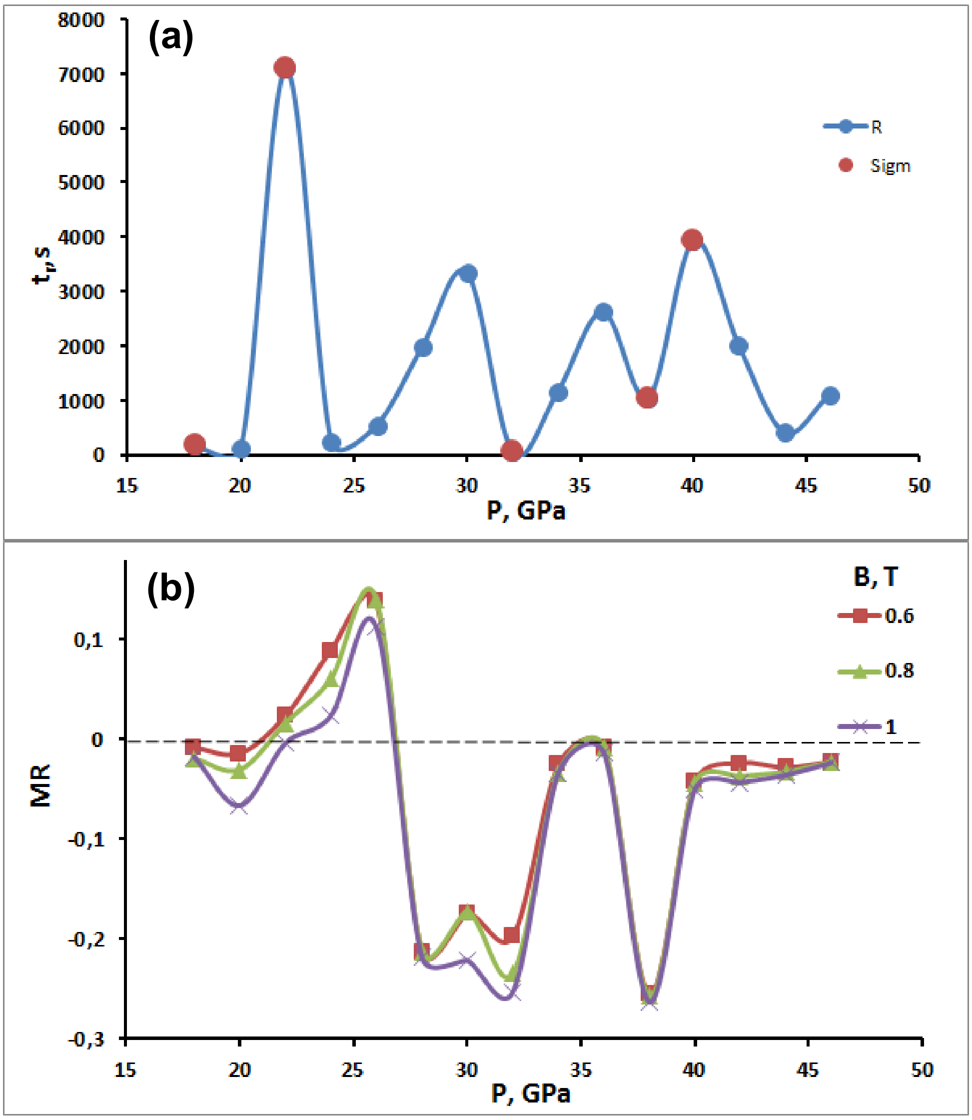

Figure 5. Resistivity relaxation time (a) and magnetoresistance at different values of magnetic field (b) as a function of pressure for $(InSe)_x(CuAsSe_2)_{1-x}$, $x = 0.05$.

and the features in the curves of magnetoresistance versus pressure can be observed in pressure ranges different from those of $CuInAsSe_3$. The significant changes in the behavior of all the investigated properties of $(InSe)_x(CuAsSe_2)_{1-x}$, $x = 0.05$, can be interpreted as manifestations of crystallographic phase transitions that are typical of materials with the sphalerite structure at atmospheric pressure [2].

Investigations of resistivity relaxation in both materials show that significant changes in the relaxation times and in the character of relaxation curves are observed in the pressure intervals corresponding to significant changes in the other studied electrical parameters. The average relaxation times were estimated using an exponential function approximation of the time profiles of resistivity or conductivity (equation 2; a is resistivity or conductivity; b_1, b_2, are constants; t_r is the relaxation time);

$$a = b_1 \cdot \exp\left(-\frac{t}{t_r}\right) + b_2. \tag{2}$$

The extrema are present at $t_r(P)$ for $(InSe)_x(CuAsSe_2)_{1-x}$, $x = 0.05$ (figure 5a), in the neighborhood of pressures corresponding to the MR value approximately equal or close to zero. These pressures may correspond to a change in the type of carriers, their concentration and the chemical potential in the process of deformation and changes in the crystal structure. Similar regularities were observed for $CuInSe_2$ and $CuInS_2$, where the changes in the type of carriers in the above mentioned pressure ranges were confirmed by the results of high-pressure thermopower investigations [2].

4. Conclusions

The analysis of the behavior of electrical properties of the polycrystalline materials $CuInAsSe_3$ and $(InSe)_{0.05}(CuAsSe_2)_{0.95}$ in the 1 Hz to 32 MHz electrical field and the study of resistivity relaxation in the DC electrical field at pressures up to 50 GPa revealed that, for each compound, the features in the curves of pressure dependence of all the physical parameters of interest were observed in the same pressure intervals. Such a behavior of the physical parameters can be due to structural transitions and a change in the electron structure.

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